

U.S. PATENT APPLICATION

OF

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FOR

HIGH PURITY TANTALUM,
PRODUCTS CONTAINING THE SAME,
AND METHODS OF MAKING THE SAME

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AND METHODS OF MAKING THE SAME

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BACKGROUND OF THE INVENTION

The present invention relates to metals, in particular tantalum, and products made
10 from tantalum as well as methods of making and processing the tantalum.

In industry, there has always been a desire to form higher purity metals for a variety
of reasons. With respect to tantalum, higher purity metals are especially desirable due to
tantalum's use as a sputtering target and its use in electrical components such as capacitors.

Thus, impurities in the metal can have an undesirable effect on the properties of the articles
15 formed from the tantalum.

When tantalum is processed, the tantalum is obtained from ore and subsequently
crushed and the tantalum separated from the crushed ore through the use of an acid solution
and density separation of the acid solution containing the tantalum from the acid solution
containing niobium and other impurities. The acid solution containing the tantalum is then
20 crystallized into a salt and this tantalum containing salt is then reacted with pure sodium in a
vessel having an agitator typically constructed of nickel alloy material, wherein tungsten or
molybdenum is part of the nickel alloy. The vessel will typically be a double walled vessel
with pure nickel in the interior surface. The salt is then dissolved in water to obtain
tantalum powder. However, during such processing, the tantalum powder is contaminated
25 by the various surfaces that it comes in contact with such as the tungsten and/or
molybdenum containing surfaces. Many contaminants can be volatilized during subsequent
melting, except highly soluble refractory metals (e.g., Nb, Mo, and W). These impurities

can be quite difficult or impossible to remove, thus preventing a very high purity tantalum product.

Accordingly, there is a desire to obtain higher purity tantalum products which substantially avoid the contaminations obtained during the processing discussed above.

5 Also, there is a desire to have a tantalum product having higher purity, a fine grain size, and/or a uniform texture. Qualities such as fine grain size can be an important property for sputtering targets made from tantalum since fine grain size can lead to improved uniformity of thickness of the sputtered deposited film. Further, other products containing the tantalum having fine grain size can lead to improved homogeneity of deformation and enhancement
10 of deep drawability and stretchability which are beneficial in making capacitors cans, laboratory crucibles, and increasing the lethality of explosively formed penetrators (EFP's). Uniform texture in tantalum containing products can increase sputtering efficiency (e.g., greater sputter rate) and can increase normal anisotropy (e.g., increased deep drawability), in preform products.

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SUMMARY OF THE PRESENT INVENTION

A feature of the present invention is to provide a high purity tantalum product exhibiting a fine grain structure and/or uniform texture.

Another feature of the present invention is to provide articles, products, and/or
20 components containing the high purity tantalum.

An additional feature of the present invention is to provide processes to make the high purity tantalum product as well as the articles, products, and/or components containing the high purity tantalum.

Additional features and advantages of the present invention will be set forth in part in the description which follows, and in part will be apparent from the description, or may be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and attained by means of the elements and combinations particularly pointed out in the description and appended claims.

To achieve these and other advantages, and in accordance with the purpose of the present invention, as embodied and broadly described herein, the present invention relates to tantalum metal having a purity of at least 99.995% and more preferably at least 99.999%. The tantalum metal preferably has a fine grain structure and/or uniform texture.

The present invention further relates to an alloy or mixture comprising tantalum, wherein the tantalum present in the alloy or mixture has a purity of at least 99.995% and more preferably at least 99.999%. The alloy or mixture (e.g., at least the tantalum present in the alloy or mixture) also preferably has a fine grain structure and/or uniform texture.

The present invention also relates to a high purity tantalum, e.g., suitable for use as a sputtering target, having a fully recrystallized grain size with an average grain size of about 150 μm or less and/or having a primary (111)-type texture substantially throughout the thickness of the tantalum and preferably throughout the entire thickness of the tantalum metal and/or having an absence of strong (100) texture bands within the thickness of the tantalum.

The present invention further relates to manufacturing plate and sheet from the above-mentioned tantalum by flat-forging the tantalum, machining into rolling slabs, annealing rolling slabs, rolling into plate or sheet, then annealing the plate or sheet. Final products such as sputtering targets can be then machined from the annealed plate or sheet.

The present invention also relates to a sputtering target comprising the above-described tantalum and/or alloy. The sputtering target can also be formed by radial forging and subsequent round processing to produce billets or slugs, which are then forged and rolled to yield discs, which can then be machined and annealed.

5 The present invention further relates to resistive films and capacitors comprising the above-described tantalum and/or alloy.

The present invention also relates to articles, components, or products which comprise at least in part the above-described tantalum and/or alloy.

Also, the present invention relates to a process of making the above-described
10 tantalum which involves reacting a salt-containing tantalum with pure sodium or other suitable salt in a reactive container or pot and an agitator which both are made from or have a liner comprising a metal or alloy thereof which has the same or higher vapor pressure as tantalum at the melting point of tantalum.

The present invention further relates to processing tantalum powder by melting the
15 tantalum powder in a high vacuum of 10^{-2} torr or more. The pressure above the melt is lower than the vapor pressures of the impurities existing in the tantalum. Preferably, the melting of the tantalum powder is accomplished by electron beam melting.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further
20 explanation of the present invention, as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1(A-B)-11(A-B) are graphs and corresponding data relating to texture gradient (incremental thickness vs. random) and log ratio (111):(100) gradients (incremental thickness vs. Ln (111/100)) of high purity tantalum plates of the present invention.

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DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention relates to a tantalum metal having a purity of at least 99.995%. Preferably, the tantalum metal has a purity of at least 99.999% and can range in purity from about 99.995% to about 99.999% or more. Other ranges include about 10 99.998% to about 99.999% and from about 99.999% to about 99.9992% and from about 99.999% to about 99.9995%. The present invention further relates to a metal alloy which comprises the high purity tantalum metal, such as a tantalum based alloy or other alloy which contains the high purity tantalum as one of the components of the alloy.

The impurities that may be present in the high purity tantalum metal are less than or 15 equal to .005% and typically comprise other body-centered cubic (bcc) refractory metals of infinite solubility in tantalum, such as niobium, molybdenum, and tungsten.

The tantalum metal and alloys thereof containing the tantalum metal preferably have a texture which is advantageous for particular end uses, such as sputtering. In other words, when the tantalum metal or alloy thereof is formed into a sputtering target having a surface 20 and then sputtered, the texture of the tantalum metal in the present invention leads to a sputtering target which is easily sputtered and, very few if any areas in the sputtering target resist sputtering. Further, with the texture of the tantalum metal of the present invention, the sputtering of the sputtering target leads to a very uniform sputtering erosion thus leading

to a sputtered film which is therefore uniform as well. It is preferred that the tantalum having any purity, but preferably a purity of at least about 99.995%, has a grain size of about 150 microns or less. Preferably, the tantalum metal is at least partially recrystallized, and more preferably at least about 80% of the tantalum metal is recrystallized and even
5 more preferably at least about 98% of the tantalum metal is recrystallized. Most preferably, the tantalum metal is fully recrystallized.

Also, it is preferred that the tantalum metal have a fine texture. More preferably the texture is such that the (100) peak intensity within any 5% incremental thickness of the tantalum is less than about 15 random, and/or has a natural log (Ln) ratio of (111):(100)
10 center peak intensities within the same increment greater than about - 4.0 (i.e., meaning, - 4.0, -3.0, -2.0, -1.5, -1.0 and so on) or has both the (100) centroid intensity and the ratio. The center peak intensity is preferably from about 0 random to about 10 random, and more preferably is from about 0 random to about 5 random. Other (100) centroid intensity ranges include, but are not limited to, from about 1 random to about 10 random and from about 1
15 random to about 5 random. Further, the log ratio of (111):(100) center peak intensities is from about - 4.0 to about 15 and more preferably from about -1.5 to about 7.0. Other suitable ranges of log ratios, include, but are not limited to, about -4.0 to about 10, and from about -3.0 to about 5.0. Most preferably, the tantalum metal has the desired purity of at least about 99.995% and the preferred grain size and preferred texture with regard to the
20 (100) incremental intensity and the (111):(100) ratio of incremental centroid intensities. The method and equipment that can be used to characterize the texture are described in Adams et al., Materials Science Forum, Vol. 157-162 (1994), pp. 31-42; Adams et al., Metallurgical Transactions A, Vol 24A, April 1993-No. 4, pp.819-831; Wright et al.,

International Academic Publishers, 137 Chaonei Dajie, Beijing, 1996 ("Textures of Material: Proceedings of the Eleventh International Conference on Textures of Materials"); Wright, Journal of Computer-Assisted Microscopy, Vol. 5, No. 3 (1993), all incorporated in their entirety by reference herein.

5 The high purity tantalum metal of the present invention can be used in a number of areas. For instance, the high purity tantalum metal can be made into a sputtering target or into chemical energy (CE) munition warhead liner which comprises the high purity metal. The high purity metal can also be used and formed into a capacitor anode or into a resistive film layer. The tantalum metal of the present invention can be used in any article or
10 component which conventional tantalum is used and the methods and means of making the various articles or components containing the conventional tantalum can be used equally here in incorporating the high purity tantalum metal into the various articles or components. For instance, the subsequent processing used in making sputtering targets, such as the backing plate, described in U.S. Patent Nos. 5,753,090, 5,687,600, and 5,522,535 can be
15 used here and these patents are incorporated in their entirety by reference herein.

 Generally, a process that can be used to make the high purity tantalum metal of the present invention involves a refining process, a vacuum melting process, and a thermal mechanical process. In this process or operation, the refining process involves the steps of extracting tantalum metal preferably in the form a powder from ore containing tantalum and
20 preferably the ore-containing tantalum selected has low amounts of impurities, especially, low amounts of niobium, molybdenum, and tungsten. More preferably, the amount of niobium, molybdenum, and tungsten is below about 10 ppm, and most preferably is below about 8 ppm. Such a selection leads to a purer tantalum metal. After the refining process,

the vacuum melting process is used to purge low melting point impurities, such as alkyls and transition metals from the tantalum while consolidating the tantalum material into a fully dense, malleable ingot. Then, after this process, a thermal mechanical process can be used which can involve a combination of cold working and annealing of a tantalum which
5 further ensures that the preferred grain size and/or preferred texture and uniformity are achieved, if desired.

The high purity tantalum metal preferably may be made by reacting a salt-containing tantalum with at least one agent (e.g., compound or element) capable of reducing this salt to the tantalum metal and further results in the formation of a second salt in a
10 reaction container. The reaction container can be any container typically used for the reaction of metals and should withstand high temperatures on the order of about 800°C to about 1,200°C. For purposes of the present invention, the reaction container or the liner in the reaction container, which comes in contact with the salt-containing tantalum and the agent capable of reducing the salt to tantalum, is made from a material having the same or
15 higher vapor pressure as tantalum at the melting point of the tantalum. The agitator in the reaction container can be made of the same material or can be lined as well. The liner can exist only in the portions of the reaction container and agitator that come in contact with the salt and tantalum. Examples of such metal materials which can form the liner or reaction container include, but are not limited to, metal-based materials made from nickel,
20 chromium, iron, manganese, titanium, zirconium, hafnium, vanadium, ruthenium, cobalt, rhodium, palladium, platinum, or any combination thereof or alloy thereof as long as the alloy material has the same or higher vapor pressure as the melting point of tantalum metal. Preferably, the metal is a nickel or a nickel-based alloy, a chromium or a chromium-based

alloy, or an iron or an iron-based alloy. The liner, on the reaction container and/or agitator, if present, typically will have a thickness of from about .5 cm to about 3 cm. Other thicknesses can be used. It is within the bounds of the present invention to have multiple layers of liners made of the same or different metal materials described above.

5 The salt-containing tantalum can be any salt capable of having tantalum contained therein such as a potassium-fluoride tantalum. With respect to the agent capable of reducing the salt to tantalum and a second salt in the reaction container, the agent which is capable of doing this reduction is any agent which has the ability to result in reducing the salt-containing tantalum to just tantalum metal and other ingredients (*e.g.* salt(s)) which can
10 be separated from the tantalum metal, for example, by dissolving the salts with water or other aqueous sources. Preferably, this agent is sodium. Other examples include, but are not limited to, lithium, magnesium, calcium, potassium, carbon, carbon monoxide, ionic hydrogen, and the like. Typically, the second salt which also is formed during the reduction of the salt-containing tantalum is sodium fluoride. Details of the reduction process
15 which can be applied to the present invention in view of the present application are set forth in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Edition, Vol 22, pp. 541-564, U.S. Patent Nos. 2,950,185; 3,829,310; 4,149,876; and 3,767,456. Further details of the processing of tantalum can be found in U.S. Patent Nos. 5,234,491; 5,242,481; and 4,684,399. All of these patents and publications are incorporated in their entirety by
20 reference herein.

The above-described process can be included in a multi-step process which can begin with low purity tantalum, such as ore-containing tantalum. One of the impurities that can be substantially present with the tantalum is niobium. Other impurities at this stage are

tungsten, silicon, calcium, iron, manganese, etc. In more detail, low purity tantalum can be purified by mixing the low purity tantalum which has tantalum and impurities with an acid solution. The low purity tantalum, if present as an ore, should first be crushed before being combined with an acid solution. The acid solution should be capable of dissolving
5 substantially all of the tantalum and impurities, especially when the mixing is occurring at high temperatures.

Once the acid solution has had sufficient time to dissolve substantially, if not all, of the solids containing the tantalum and impurities, a liquid solid separation can occur which will generally remove any of the undissolved impurities. The solution is further purified by
10 liquid-liquid extraction. Methyl isobutyl ketone (MIBK) can be used to contact the tantalum rich solution, and deionized water can be added to create a tantalum fraction. At this point, the amount of niobium present in the liquid containing tantalum is generally below about 25 ppm.

Then, with the liquid containing at least tantalum, the liquid is permitted to
15 crystallize into a salt with the use of vats. Typically, this salt will be a potassium tantalum fluoride salt. More preferably, this salt is K_2TaF_7 . This salt is then reacted with an agent capable of reducing the salt into 1) tantalum and 2) a second salt as described above. This compound will typically be pure sodium and the reaction will occur in a reaction container described above. As stated above, the second salt byproducts can be separated from the
20 tantalum by dissolving the salt in an aqueous source and washing away the dissolved salt. At this stage, the purity of the tantalum is typically 99.50 to 99.99% Ta.

Once the tantalum powder is extracted from this reaction, any impurities remaining, including any contamination from the reaction container, can be removed through melting

of the tantalum powder.

The tantalum powder can be melted a number of ways such as a vacuum arc remelt or an electron beam melting. Generally, the vacuum during the melt will be sufficient to remove substantially any existing impurities from the recovered tantalum so as to obtain high purity tantalum. Preferably, the melting occurs in a high vacuum such as 10^{-4} torr or more. Preferably, the pressure above the melted tantalum is lower than the vapor pressures of the metal impurities in order for these impurities, such as nickel and iron to be vaporized. The diameter of the cast ingot should be as large as possible, preferably greater than 9 1/2 inches. The large diameter assures a greater melt surface to vacuum interface which enhances purification rates. In addition, the large ingot diameter allows for a greater amount of cold work to be imparted to the metal during processing, which improves the attributes of the final products. Once the mass of melted tantalum consolidates, the ingot formed will have a purity of 99.995% or higher and preferably 99.999% or higher. The electron beam processing preferably occurs at a melt rate of from about 300 to about 800 lbs. per hour using 20,000 to 28,000 volts and 15 to 40 amps, and under a vacuum of from about 1×10^{-3} to about 1×10^{-6} Torr. More preferably, the melt rate is from about 400 to about 600 lbs. per hour using from 24,000 to 26,000 volts and 17 to 36 amps, and under a vacuum of from about 1×10^{-4} to 1×10^{-5} Torr. With respect to the VAR processing, the melt rate is preferably of 500 to 2,000 lbs. per hour using 25-45 volts and 12,000 to 22,000 amps under a vacuum of 2×10^{-2} to 1×10^{-4} Torr, and more preferably 800 to 1200 lbs. per hour at from 30 to 60 volts and 16,000 to 18,000 amps, and under a vacuum of from 2×10^{-2} to 1×10^{-4} Torr.

The high purity tantalum ingot can then be thermomechanically processed to

produce the high purity tantalum containing product. The fine, and preferably fully recrystallized, grain structure and/or uniform texture is imparted to the product through a combination of cold and/or warm working and in-process annealing. The high purity tantalum product preferably exhibits a uniform texture of mixed or primary (111) throughout its thickness as measured by orientation imaging microscopy (OIM) or other acceptable means. With respect to thermomechanical processing, the ingot can be subjected to rolling and/or forging processes and a fine, uniform microstructure having high purity can be obtained. The high purity tantalum has an excellent fine grain size and/or a uniform distribution. The high purity tantalum preferably has an average recrystallized grain size of about 150 microns or less, more preferably about 100 microns or less, and even more preferably about 50 microns or less. Ranges of suitable average grain sizes include from about 25 to about 150 microns; from about 30 to about 125 microns, and from about 30 to about 100 microns.

The resulting high purity metal of the present invention, preferably has 10 ppm or less metallic impurities and preferably 50 ppm or less O₂, 25 ppm or less N₂, and 25 ppm or less carbon. If a purity level of about 99.995 is desired, then the resulting high purity metal preferably has metallic impurities of about 50 ppm or less, and preferably 50 ppm or less O₂, 25 ppm or less N₂, and 25 ppm or less carbon.

With respect to taking this ingot and forming a sputtering target, the following process can be used. In one embodiment, the sputtering target made from the high purity tantalum metal can be made by mechanically or chemically cleaning the surfaces of the tantalum metal, wherein the tantalum metal has a sufficient starting cross-sectional area to permit the subsequent processing steps described below. Preferably the tantalum metal has a

cross-sectional area of at least 9 1/2 inches or more. The next step involves flat forging the tantalum metal into one or more rolling slabs. The rolling slab(s) has a sufficient deformation to achieve substantially uniform recrystallization after the annealing step immediately following this step as described below. The rolling slab(s) is then annealed in vacuum and at a sufficient temperature to achieve at least partial recrystallization of the rolling slab(s). Preferred annealing temperatures and times are set forth below and in the examples. The rolling slab(s) is then subjected to cold or warm rolling in both the perpendicular and parallel directions to the axis of the starting tantalum metal (e.g., the tantalum ingot) to form at least one plate. The plate is then subjected to flattening (e.g., level rolling). The plate is then annealed a final time at a sufficient temperature and for a sufficient time to have an average grain size of equal to or less than about 150 microns and a texture substantially void of (100) textural bands. Preferably, no (100) textural bands exist. The plate can then be mechanically or chemically cleaned again and formed into the sputtering target having any desired dimension. Typically, the flat forging will occur after the tantalum metal is placed in air for at least about 4 hours at temperatures ranging from ambient to about 370°C. Also, preferably before cold rolling, the rolling slabs are annealed at a temperature (e.g., from about 950°C to about 1500°C) and for a time (e.g., from about 1/2 hour to about 8 hours) to achieve at least partial recrystallization of the tantalum metal. Preferably the cold rolling is transverse rolling at ambient temperatures and the warm rolling is at temperatures of less than about 370°C.

With respect to annealing of the tantalum plate, preferably this annealing is in a vacuum annealing at a temperature and for a time sufficient to achieve complete recrystallization of the tantalum metal. The examples in this application set forth further

preferred details with respect to this processing.

Another way to process the tantalum metal into sputtering targets involves mechanically or chemically clean surfaces of the tantalum metal (e.g., the tantalum ingot), wherein the tantalum metal has a sufficient starting cross-sectional area to permit the subsequent processing as described above. The next step involves round forging the tantalum metal into at least one rod, wherein the rod has sufficient deformation to achieve substantially uniform recrystallization either after the annealing step which occurs immediately after this step or the annealing step prior to cold rolling. The tantalum rod is then cut into billets and the surfaces mechanically or chemically cleaned. An optional annealing step can occur afterwards to achieve at least partial recrystallization. The billets are then axially forged into preforms. Again, an optional annealing step can occur afterwards to achieve at least partial recrystallization. However, at least one of the optional annealing steps or both are done. The preforms are then subjected to cold rolling into at least one plate. Afterwards, the surfaces of the plate(s) can be optionally mechanically or chemically clean. Then, the final annealing step occurs to result in an average grain size of about 150 microns or less and a texture substantially void of (100) textural bands, if not totally void of (100) textural bands. The round forging typically occurs after subjecting the tantalum metal to temperatures of about 370°C or lower. Higher temperatures can be used which results in increased oxidation of the surface. Preferably, prior to forging the billets, the billets are annealed. Also, the preforms, prior to cold rolling can be annealed. Typically, these annealing temperatures will be from about 900°C to about 1200°C. Also, any annealing is preferably vacuum annealing at a sufficient temperature and for a sufficient time to achieve recrystallization of the tantalum metal.

Preferably, the sputtering targets made from the high purity tantalum have the following dimensions: a thickness of from about 0.080 to about 1.50", and a surface area from about 7.0 to about 1225 square inches.

The high purity tantalum preferably has a primary or mixed (111) texture, and a
5 minimum (100) texture throughout the thickness of the sputtering target, and is sufficiently void of (100) textural bands.

The present invention will be further clarified by the following examples, which are intended to be purely exemplary of the present invention.

EXAMPLES

10 **Example 1**

Numerous sublots of sodium-reduced commercial-grade tantalum powder, each weighing about 200-800 lbs., were chemically analyzed for suitability as 99.999% Ta feedstock for electron beam melting. Representative samples from each powder lot were analyzed by Glow Discharge Mass Spectrometry (GDMS): powder sublots having
15 combined niobium (Nb), molybdenum (Mo), and tungsten (W) impurity content less than 8 ppm were selected for melting.

The selected Ta powder sublots were then blended in a V-cone blender to produce a homogeneous 4000 pound powder master lot, which was again analyzed by GDMS to confirm purity. Next, the powder was cold isostatically pressed (CIP'ed)
20 into green logs approximately 5.5"-6.5" in diameter, each weighing nominally 300 pounds. The pressed logs were then degassed by heating at 1450°C for 2 hours at a vacuum level of about 10^{-3} - 10^{-5} torr. For this operation, the logs were covered with tantalum sheets to prevent contamination from the furnace elements.

The degassed logs were then side fed into a 1200KW EB furnace and drip melted at a rate of 400 lbs./hr. into a 10" water-cooled copper crucible under a vacuum less than 10^{-3} torr. Once cooled, the resulting first-melt ingot was inverted, hung in the same furnace, and remelted using the same EB melting parameters. The 2nd melt ingot
5 was again inverted and remelted a third time, but into a 12" crucible at a melt rate of 800 lbs./hr.

A sample was taken from the sidewall of the resulting ingot for chemical analysis by Glow Discharge Mass Spectrometry (GDMS). Results confirmed that the Ta ingot was 99.9992% pure.

10 Example 2

A potassium fluotantalate (K_2TaF_7) was obtained and upon spark source mass spec analysis, the K_2TaF_7 exhibited 5 ppm or less niobium. Levels of Mo and W were also analyzed by spectrographic detection and levels were below 5 ppm for Mo and below 100 ppm for W. In particular, the K_2TaF_7 had levels of Nb of 2 ppm or less, of Mo of less than
15 1 ppm and of W of less than or equal to 2 ppm. In each sample, the total recorded amount of Nb, Mo, and W was below 5 ppm. Four lots of 2,200 lbs. each were analyzed.

One of the lots was transferred to KDEL reactor which used a pure nickel vessel and a Hastelloy X agitator. The Hastelloy X agitator contained 9% Mo and 0.6% W. The shaft and paddles of the agitator were then shielded with 1/16" nickel sheet using welding to
20 clad all surfaces exposed to the reaction.

A standard sodium reduction process was used except as noted below. The lot was subjected to the agitator in the presence of pure sodium to form tantalum powder. The tantalum powder was then washed with water and subjected to acid treating and then steam

drying and then screening to -100 mesh.

A sample from each batch was then submitted for glow discharge mass spec analysis. The two tables (Tables 1 and 2) below show the starting analysis for the K_2TaF_7 and the final analysis of the tantalum recovered.

5

Table 1

K_2TaF_7 Spark Source Mass Spec (SSMS) Analysis

(metal to salt basis)

Sample Number	Nb (ppm)	Mo (ppm)	W (ppm)	TOTAL (ppm)
1	2	< 1	≤ 2	< 5
2	1	< 1	≤ 2	< 4
3	2	< 1	≤ 2	< 5
4	1	< 1	≤ 2	< 4

10

Table 2

Ta Powder Glow Discharge Mass Spec (GDMS) Analysis

Sample Number	Nb (ppm)	Mo (ppm)	W (ppm)	TOTAL (ppm)
5	1.4	0.38	0.27	2.05
6	1.2	0.30	0.50	2.00
7	1.0	0.25	0.29	1.54
8	1.1	0.15	0.28	1.53

As can be seen in the above tables, a high purity tantalum powder suitable for electron beam melting into an ingot can be obtained and purities on the order of 99.999% purity can be obtained by the processing shown in Example 1.

Example 3.

Two distinct process methodologies were used. First, a 99.998% pure tantalum

ingot was used which was subjected to three electron beams melts to produce a 12 inch nominal diameter ingot. The ingot was machined clean to about 11 ½ inch diameter and then heated in air to about 260°C for 4-8 hours. The ingot was then flat forged, cut, and machined into slabs (approximately 4 inch by 10 inch with a length of approximately 28 inch to 32 inch) and then acid cleaned with HF/HNO₃ /water solution. The slabs were annealed at 1050, 1150, and 1300°C under vacuum of 5 X 10⁻⁴ Torr for 2 hours, then cold rolled into plate stock of 0.500 and 0.250" gauge. This cold rolling was accomplished by taking a 4 inch thick by 10 inch wide by 30 inch long slab and rolling it perpendicular to the ingot axis at 0.200 inch per pass to 31 inches wide. The plate was then rolled parallel to the ingot axis at 0.100 inch per pass to 0.650 inch thick or 0.500 inch thick. Both rollings were done on a 2-High breakdown rolling mill. Each of the plates were rolled by multiples passes of 0.050 inch per pass and then 0.025 inch per pass with final adjustments to meet a finish gauge of 0.500 inch plate or 0.250 inch plate, using a four high finishing rolling mill. The plates were then subjected to a final annealing at temperatures of from 950 - 1150°C.

The alternative process began with a 99.95 % pure Ta which was subjected to three electron beam melts to produce an ingot as described above prior to being forged. The ingot was then round forged using a GFM rotary forge to 4" diameter after multiples passes of about 20% reduction in area per pass. From this intermediate stock, 4 billets (3.75" Ø x 7" long) were machined, and 2 billets (labeled A and B) were annealed at 1050°C while billets C and D remained unannealed. Next, the billets were upset forged to preforms of height of 2.5", after which preforms A and C were annealed at 1050°C. The preforms were then clock rolled to a thickness of about

0.400" to yield discs of a diameter of approximately 14". This was accomplished by taking multiple passes of 0.200 inch per pass to about 0.5250 inch thick. The discs were then rolled to about 0.5 inch thick by multiple passes of 0.100 inch per pass. Then, the discs were clocked rolled on a four high finishing mill in three passes of 0.050 inch, 0.025 inch, and 0.015 inch reductions per pass to yield a disc of about 0.400 inch thick by about 14 inch diameter. A quarter of the disc was cut into four wedges and final annealed at temperatures of 950-1100°C. Table 4 below summarizes this processing.

Metallographic and texture analysis was conducted on longitudinal sections of the plate material (measurement face parallel to the final rolling direction) and on radial sections of the forged and rolled discs (measurement face parallel to the radius of the discs).

METALLURGICAL ANALYSIS

Grain size and texture were measured along the longitudinal or radial directions of samples taken from rolled plate and forged and rolled discs, respectively. Grain size was measured using ASTM procedure E-112. Results from the annealing studies on products produced via the flat and round processes are given in Tables 3 and 4, respectively. Intermediate annealing treatments had no noticeable influence on the grain size of the finished product. Also, for plate, the final grain sizes of 0.500 and 0.250" thick tantalum were comparable. The only variable found to significantly effect the grain size of the materials was the final anneal temperature: the higher the final anneal temperature, the larger the resulting grain size.

In plate, grain sizes of ASTM 6.5 - 7.0 were measured in samples from product annealed at 1000 and 950°C. However, each of these samples showed evidence of elongated and/or unrecrystallized regions at or near the surface, and recrystallization values were reported to be 98-99%. For plates annealed at 1050, 1100, and 1150°C, 5 ASTM grain sizes ranged from 5.3 to 3.7, with all samples being 100% recrystallized.

For the round-processed discs, all samples were reported to be 100% recrystallized, with the exception of Disc C annealed at 950°C which was 99% recrystallized. Grain sizes of ASTM 7.1-7.2, 6.1-6.8, and 5.9-5.9 were measured in the disc samples annealed at 950, 1000, and 1050°C, respectively. Annealing at 10 1100°C produced grain sizes of ASTM 4.0-4.5.

For both processes, these findings demonstrate that a fully recrystallized grain size of 50 μm or finer is achievable using either the plate rolling or the billet forging process at a preferred final anneal temperature of from about 950 to about 1050°C. Should the unrecrystallized areas be limited to only the surface regions of the plate, 15 then they can be removed by machining.

Texture Measurement Technique: A limited number of samples (chosen based on metallurgical results) were used for texture analysis. Mounted and polished samples, previously prepared for metallurgical analysis, were employed as texture samples after being given a heavy acid etch prior to texture measurement. Orientation 20 Imaging Microscopy (OIM) was chosen as the method of texture analysis because of its unique ability to determine the orientation of individual grains within a polycrystalline sample. Established techniques such as X-ray or neutron diffraction would have been unable to resolve any localized texture variations within the thickness of the tantalum

materials.

For the analysis, each texture sample was incrementally scanned by an electron beam (within an SEM) across its entire thickness; the backscatter Kikuchi patterns generated for each measurement point was then indexed using a computer to determine the crystal orientation. From each sample, a raw-data file containing the orientations for each data point within the measurement grid array was created. These files served as the input data for subsequently producing grain orientation maps and calculating pole figures and orientation distribution functions (ODFs).

By convention, texture orientations are described in reference to the sample-normal coordinate system. That is, pole figures are "standardized" such that the origin is normal to the plate surface, and the reference direction is the rolling (or radial) direction; likewise, ODFs are always defined with respect to the sample-normal coordinate system. Terminology such as "a (111) texture" means that the (111) atomic planes are preferentially oriented to be parallel (and the (111) pole oriented to be normal) with the surface of the plate. In the analyses, the crystal orientations were measured with respect to the sample longitudinal direction. Therefore, it was necessary to transpose the orientation data from the longitudinal to sample-normal coordinate system as part of the subsequent texture analysis. These tasks were conducted through use of computer algorithms.

Grain Orientation Maps: Derived from principles of presenting texture information in the form of inverse pole figures, orientation maps are images of the microstructure within the sample where each individual grain is "color-coded " based on its crystallographic orientation relative to the normal direction of the plate of disc

from which it was taken. To produce these images, the crystal axes for each grain (determined along the longitudinal direction of the texture sample by OIM) were tilted 90° about the transverse direction so to align the crystal axes to the normal direction of the sample. Orientation maps serve to reveal the presence of texture bands or gradients through the thickness on the product; in tantalum, orientation maps have shown that large, elongated grains identified by optical microscopy can be composed of several small grains with low-angle grain boundaries.

Analysis of the Texture Results: OIM scans were taken along the thickness of each sample provided; for the 0.500" plate samples, separate measurements were made for the top and the bottom portions of the plate and reported separately.

The orientation maps were visually examined to qualitatively characterize the texture uniformity through the sample thickness. To attain a quantifiable description of the texture gradients and texture bands in the example materials, the measured EBSD data was partitioned into 20 subsets, with each representing a 5% increment of depth through the thickness of the sample. For each incremental data set, an ODF was first calculated, then (100) and (111) centroid intensities determined numerically using techniques reported elsewhere. The equipment and procedures described in S. Matthies et al., Materials Science Forum, Vol. 157-162 (1994), pp. 1647-1652 and S. Matthies et al., Materials Science Forum, Vol. 157-162 (1994), pp. 1641-1646 were applied, and these publications are incorporated in their entirety herein by reference. The texture gradients were then described graphically by plotting the (100) and (111) intensities, as well as the log ratio of the (100):(111), as a function depth of the sample. These results are set forth in Figures 1 (A and B) through Figures 11 (A and

B).

The heavy-gauge tantalum plate exhibited the most uniform through-thickness texture; the only sample containing texture bands was that processed with a slab anneal of 1300°C and a final anneal of 1000°C. In addition, the 0.500" plate materials also
5 had a relative weak (most random) texture base on pole figure and ODF analysis. Compared to the heavy plate, the 0.250' sheets contained a slight to moderate texture gradient and some evidence of texture banding. Also, the thin-gauge plates showed a more defined (111) texture in the ODFs and an increased prominence of (100).

The greatest variability in terms of texture uniformity and banding was found in
10 the forged and rolled discs. Unlike the metallurgical properties, the texture of forged and rolled discs was effected by the use of intermediate annealing. For discs A, B, and C, each of which were processed with one or two intermediate annealing steps, the texture gradients ranged from negligible to strong (depending to processing parameters) with slight – if any – banding. However, for disc D, which was worked from ingot to
15 final discs without intermediate annealing, the resultant product contained less desirable strong texture gradients and sharp texture bands. Similarly, disc C, which was also forged from unannealed billet but then annealed prior to cold rolling, also showed a strong texture gradient and banding in the sample final annealed at 950°C. For disc C, increasing the final anneal temperature to 1100°C acted to diminish the gradient,
20 eliminated the bands, but strengthening the intensity of (100) texture component. These effects from increasing final annealing temperatures were also evident, but to a lesser degree, in both the other disc materials and the heavy gauge plate.

From the microstructural and textural observations, the following conclusions could be made regarding the optimum processing for fabricating tantalum sputtering targets:

- 5 • For flat products, slab anneal temperatures preferably do not exceed 1150°C (1050°C is more preferred) and the final anneal temperature is preferably kept at 950-1000°C, more preferably 1000°C. The resulting product is characterized as having a recrystallized average grain size of less 50 μm . and a (100) incremental intensity of less than 15 random and a log ratio of (111):(100) of less than -4.0.
- 10 • For round processing, billets preferably are annealed prior to forging and rolling into disc without use of an intermediate anneal at preform level. Final anneal temperature is preferably 950-1100°C., and more preferably is 1050°C. The resulting product is characterized as having a recrystallized average grain size below 50 μm , and a (100) incremental intensity of less
15 than 15 random and a log ratio of (111):(100) of less than -4.0.

Table 3 - - - Metallurgical Characteristics Process

Slab Anneal Temperature (°C)		1050		1150		1300	
Gauge of Plate Produced from Slab		.250"	.500"	.250"	.500"	.250"	.500"
Plate Anneal Temperature (°C)		ASTM Grain Size	% Recry.	ASTM Grain Size	% Recry.	ASTM Grain Size	% Recry.
950		7.0	98	7.0	98	7.0	98
1000		6.5	99	6.5	99	6.5	99
1050		4.5	100	4.5	100	4.5	100
1050		5.0	100	4.5	100	5.0	100
1100		4.5	100	4.5	100	4.5	100
1150		4.0	100	4.0	100	4.0	100

Note: Material Purity was 99.998 % Ti

Table 4

BILLET A	BILLET B	BILLET C	BILLET D	PC. WEIGHT	
<u>Anneal 1050 C</u>	<u>Anneal 1050 C</u>	<u>Unannealed</u>	<u>Unannealed</u>	46.4 lbs	7" Long
Upset Forge 2.5" Thick	Upset Forge 2.5" Thick	Upset Forge 2.5" Thick	Upset Forge 2.5" Thick		6.25" Diameter
Anneal 1050C		Anneal 1050C			
Machine Clean	Machine Clean	Machine Clean	Machine Clean	42 lbs	6" Diameter
X-Roll to Gauge 0.400"	X-Roll to Gauge 0.400"	X-Roll to Gauge 0.400"	X-Roll to Gauge 0.400"		15" Diameter
Saw Cut Quarters	Saw Cut Quarters	Saw Cut Quarters	Saw Cut Quarters	10.5 lbs/qtr.	
Anneal Study	Anneal Study	Anneal Study	Anneal Study		

ANNEAL ASTM GRAIN
TEMP(°C) SIZE (REX)

950	7.1 (100%)	7.2 (100%)	7.1 (99%)	7.2 (100%)
1000	6.1 (100%)	6.5 (100%)	5.9 (100%)	6.8 (100%)
1050	5.8 (100%)	5.9 (100%)	5.9 (100%)	5.9 (100%)
1100	4.5 (100%)	4.5 (100%)	4.5 (100%)	4.0 (100%)

REX = % Recrystallization

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the present specification and practice of the present invention disclosed herein. It is intended that the present specification and examples be considered as exemplary only with a true scope and spirit of the invention being indicated by the following claims.

100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200